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Damarane Triterpene from *Cleome arabica*.

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ABSTRACT

A damarane triterpene was isolated from the aerial parts of *Cleome arabica* L. (Capparaceae). The structure of the compound was elucidated by extensive spectroscopic methods including 1D- [¹H and ¹³C] and 2D- NMR experiments [COSY, HMQC, HMBC] as well as HRMALDITOFMS analysis.

Keywords: *Cleome arabica*, Damarane triterpene

INTRODUCTION

In Egyptian flora, about ten species of the genus *Cleome* (Capparaceae) have been recorded. Some of them showed medical values as an anthelmintic and a counterirritant in chronic painful joints and folk remedy for infantile convulsions (1–3). Chemical investigations of some *Cleome* species led to isolation and identification of triterpenoids, nor triterpenoids and furanolignans (4–7). The aerial parts of four *Cleome* species were investigated for their surface flavonoids, affording ten methylated flavonoids as 5,7,4'-trihydroxy-3-methoxyflavone (isokaempferide), 5,7,4'-trihydroxy-3,3'-dimethoxyflavone, 5,7,4'-trihydroxy-6,3'-dimethoxyflavone (jaceosidin), 5,4'-dihydroxy-3,6,7-trimethoxy-flavone (penduletin), 5,7,3',4'-tetrahydroxy-3,6-dimethoxyflavone (axillarin), 5,7,4'-trihydroxy-6,3',5'-trimethoxyflavone, 5,4'-dihydroxy-3,6,7,3'-tetramethoxyflavone (chryso splenetin), 5,3'-dihydroxy-3,6,7,4',5'-pentamethoxyflavone, 5,4'-

dihydroxy-3,6,7,8,3'-pentamethoxyflavone and 5-hydroxy-3,6,7,3',4',5'-hexamethoxyflavone (8). Here we wish to report the isolation and elucidation of a damarane type triterpene (1) from *Cleome arabica* L.

MATERIALS AND METHODS

General

NMR spectra were measured with a Bruker AMX-400 spectrometer, with TMS as an internal standard. CC: Silica gel (Merck, 60–120 mesh) and Sephadex LH-20 (Pharmacia). TLC and Preparative TLC: Silica gel 60 GF₂₅₄ (Merck). The compound was visualized either by spraying with vanillin reagent or under UV lamp.

Plant material

Cleome arabica was collected in 2003 from El-Minia, Egypt. A voucher specimen of the collection was identified by

Prof. Mohamed Jaber and was deposited in the Department of Botany, Aswan Faculty of Science, Egypt.

Extraction and isolation

Air dried and powdered aerial parts (300 g) of *Cleome arabica* were extracted with CH_2Cl_2 at room temperature for 24 h. The extract was concentrated *in vacuo* to give a residue (25 g), which was chromatographed by using flash column chromatography on a silica gel with *n*-hexane- CH_2Cl_2 step-gradient. The CH_2Cl_2 fraction (100 %) was carefully chromatographed on a Sephadex LH-20 column eluted with *n*-hexane- CH_2Cl_2 -MeOH (7: 4: 0.5) with increasing the polarity to give a damarane triterpeneoid, compound **1** (20 mg).

RESULTS AND DISCUSSION

The methylene chloride extract of the air-dried aerial parts of *C. arabica* was chromatographed on silica gel and Sephadex LH-20 columns to give a triterpenoid type damarane (**1**). The low resolution mass spectrum showed the molecular ion peak $[\text{M}]^+$ at $m/z = 474$. The HRMALDITOFMS exhibited the molecular ion peak $[\text{M} + \text{Na}]^+$ at $m/z = 497.3607$ (calcd. 497.3608), in accord with the molecular formula of $\text{C}_{30}\text{H}_{52}\text{O}_5$. The structure of compound **1** was determined from careful investigation of 1D and 2D NMR measurements. The ^1H NMR spectrum of compound **1** revealed the presence of seven tertiary methyl singlets at δ 0.84, 1.13, 1.20, 1.12, 0.98, 1.02 and 0.88, each integrating for 3H. Additionally, it showed the oxygenated methylene protons as a pair doublet of doublets at δ 3.73 ($J = 8.8, 2.2$ Hz) and 4.24 ($J = 8.8, 2.2$ Hz), correlated in ^1H - ^{13}C COSY with one carbon signal at δ 68.0, C-19. Also, it showed the oxygenated methine proton as a triplet signal at δ 3.73 ($J = 7.5$) correlated in ^1H - ^{13}C COSY with a carbon signal at δ 83.2, C-24. The latter proton showed correlation in ^1H - ^1H COSY with multiplet signals at δ 1.75 and 1.90, H-23. Moreover the ^1H -NMR revealed the presence of several multiple signals for most protons. The ^{13}C NMR data (Table 1) revealed the presence of thirty carbon atoms and their multiplicities (by DEPT analysis) confirmed the number of hydrogen atoms of the formula given above. The carbon atoms were assigned as seven methyl carbons at $\delta = 16.1, 23.4, 27.4, 24.3, 18.6, 26.9, 15.3$ (C-18, C-21, C-26, C-27, C-28, C-29, C-30), ten methylene carbons at $\delta = 35.6, 29.6, 22.7, 31.4, 27.5, 25.6, 33.4, 19.9, 68.0, 26.3$ (C-1, C-2, C-6, C-7, C-11, C-12, C-15, C-16, C-19, C-23), five methine carbons at δ 50.0, 43.2, 45.4, 49.4, 83.2 (C-5, C-9, C-13, C-17, C-24) and seven quaternary carbons at $\delta = 98.5, 40.5, 49.6, 35.5, 39.3, 86.2, 71.5$ (C-3, C-4, C-8, C-10, C-14, C-20, C-25). Furthermore,

Table 1. ^1H NMR and ^{13}C NMR spectral data of compound **1** (400 MHz, 125 MHz, CDCl_3 , TMS as internal standard).

No.	δ_{H}	δ_{C}	HMBC
1 α 1 β	2.17 m 1.17 m	35.6 t	C-2, C-5, C-10, C-19
2 α 2 β	2.13 m 1.70 m	29.6 t	C-1
3	—	98.5 s	
4	—	40.5 s	
5 α	1.20 m	50.0 d	
6	1.00 m 1.63 m	22.7 t	
7	1.38 m 1.15 m	31.4 t	
8	—	49.6 s	
9 α	1.58 m	43.2 d	
10	—	35.5 s	
11	1.78 m 1.10 m	27.5 t	C-12
12	1.48 m 1.77 m	25.6 t	
13	1.47 m	45.4 d	
14	—	39.3 s	
15	1.30 m 1.45 m	33.4 t	C-13, C-14, C-16, C-30
16	1.65 m 1.45 m	19.9 t	
17 α	1.80 m	49.4 d	
18 β	0.84 s	16.1 q	C-7, C-8, C-9, C-14
19 α	3.73 dd (8.8, 2.2)	68.0 t	C-5, C-10,
19 β	4.24 dd (8.8, 2.2)		
20	—	86.2 s	
21	1.13 s	23.4 q	C-17, C-20, C-22
22	1.68 m 1.62 m	36.0 t	
23	1.90 m 1.75 m	26.3 t	C-22
24	3.73 t (7.5)	83.2 d	C-26, C-27
25	—	71.5 s	
26	1.20 s	27.4 q	C-24, C-25, C-27
27	1.12 s	24.3 q	C-24, C-25, C-26
28 β	0.98 s	18.6 q	C-3, C-4, C-5, C-29
29 α	1.02 s	26.9 q	C-4, C-5, C-28
30 α	0.88 s	15.3 q	C-8, C-13, C-14, C-15

all proton and carbon signals were determined by ^1H - ^1H COSY, HMQC and HMBC (Table 1). Confirmation the structure of compound **1** was given by the results of the 2D hetero nuclear multiple bond correlation [HMBC] analysis (Table 1, Fig. 1). The most important correlations were observed between H-1 (δ_{H} 2.17 m) with C-2 (δ_{C} 29.6), C-5 (δ_{C} 50.0), C-10 (δ_{C} 35.5); H-15 (δ_{H} 1.30 m) with C-13 (δ_{C} 45.4), C-14 (δ_{C} 39.3), C-16 (δ_{C} 19.9), C-17 (δ_{C} 49.4), C-30 (δ_{C} 15.3), H-18 (δ_{H} 0.84 s) with C-7 (δ_{C} 31.4), C-8 (δ_{C} 49.6), C-9 (δ_{C} 43.2), C-14 (δ_{C} 39.3); H-19 (δ_{H} 4.24 dd) with C-1 (δ_{C} 35.6), C-5 (δ_{C} 50.0), C-10 (δ_{C} 35.5); H-21 (δ_{H} 1.13 s) with C-17 (δ_{C} 49.4), C-20 (δ_{C} 86.2), C-22 (δ_{C} 36.0); H-23 (δ_{H} 1.90 m) with C-22 (δ_{C} 36.0); H-24 (δ_{H} 3.73 dd) with C-26 (δ_{C} 27.4), C-27 (δ_{C} 24.3); H-26 (δ_{H} 1.20 s) with C-24 (δ_{C} 83.2), C-25 (δ_{C} 71.5), C-27 (δ_{C} 24.3) and H-28 (δ_{H} 0.98 s) with C-3 (δ_{C} 98.5), C-4 (δ_{C} 40.5), C-5 (δ_{C} 50.0), C-29 (δ_{C} 26.9). The stereochemistry of **1** was deduced from the chemical shifts and the values of coupling constants and confirmed by the NOESY spectrum with inspection of Drieding models. The NOESY spectrum indicated clear effects between H-30 α (δ_{H} 0.88, s) and H-17 (δ_{H} 1.80, m), between H-18 β (δ_{H} 0.88, s) and H-17 (δ_{H} 1.80, m), between H-18 β (δ_{H} 0.84, s) and H-19 (δ_{H} 4.24, dd) as well

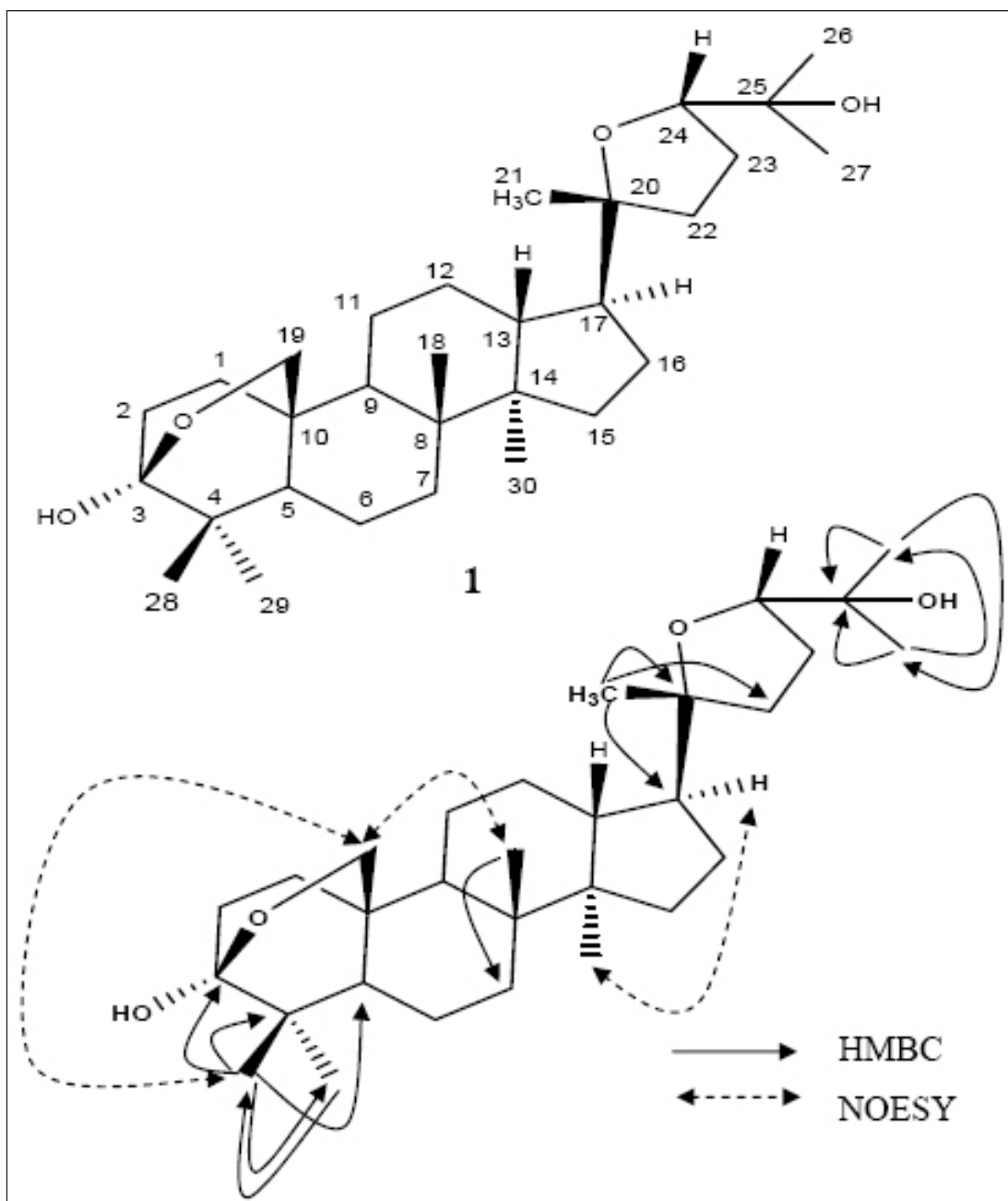


Figure 1. Selected correlations of HMBC and NOESY of compound 1

as between H-29 α (δ_{H} 1.02, s) and H-1 (δ_{H} 2.17, m), H-2 (δ_{H} 2.13, m). All previous data proved that compound 1 was a rare damarane triterpene, isolated for the first time from *Cleome arabica* [11].

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